

Thursday Afternoon, November 3, 2011

Thin Film Division

Room: 110 - Session TF+EM+SS-ThA

Applications of Self Assembled Monolayers

Moderator: M.R. Linford, Brigham Young University

2:00pm **TF+EM+SS-ThA1 Organic Monolayers on Silicon-rich Substrates: Methods and Mechanisms**, *H. Zuilhof*, Wageningen University, Netherlands **INVITED**

SAMs on silicon-containing substrates including silicon, silicon nitride and glass widely expand the applicability of such materials. The presentation will focus on 3 recent developments:

1) The surface modification of H-terminated Si has functioned as a stepping-stone for the construction of a wide-range of hybrid materials. Recent synthetic improvements and detailed mechanistic studies have shown how to optimally construct such modified substrates. These results will be presented in the light of further developments.

2) Silicon nitride can be modified by covalent SAM attachment to achieve chemically highly robust systems. Biofunctionalization thereof with oligosaccharides and antibodies provides novel diagnostic applications in terms of specific bacterial capture in combination with generally antifouling substrates when combined with lithographic structuring of the material. Proof-of-principle and remaining challenges will be demonstrated based on recent experimental progress.

3) A photochemical method we recently developed to modify glass (SiO₂), and the application thereof within the field of modified glass microchannels will be shown, e.g. via the on-chip embedding of enzymatic cascade reactions using a combination of local SAM attachment and DNA-enzyme hybrids. Finally, generalizations to the modification of other oxidic surfaces will be provided.

Key references:

H. Zuilhof and co-workers, *J. Am. Chem. Soc.* **2011**, *133*, 4998–5008.

H. Zuilhof, J. C. M. Van Hest and co-workers *Chemical Science* **2011**, *2*, in press (DOI: 10.1039/C1SC00146A).

H. Zuilhof and co-workers, *Angew Chem.* **2011**, *50*, in press (DOI: 10.1002/anie.201100835).

2:40pm **TF+EM+SS-ThA3 Molecularly Modulated Electrical Transport at Chemically Passivated Silicon Surfaces**, *G. Dubey*, NRC-SIMS, Canada, *F. Rosei*, INRS-EMT, Canada, *G.P. Lopinski*, NRC-SIMS, Canada

Adsorption of charged or polar species on semiconductor surfaces can modulate the electrical properties through long-range field effects. Hydrogen-terminated silicon-on-insulator (SOI-H) is an interesting model system for investigating this sensitivity to surface processes [1,2]. Accumulation mode SOI-H pseudo-MOSFETs [3] have been used to probe molecular adsorption and reaction events. Current-voltage characteristics of such *n*-channel devices are found to be sensitive to the environment, with the accumulation threshold voltage, or flat-band voltage (V_{FB}), exhibiting large reversible changes upon cycling between ambient atmosphere, high vacuum ($<10^{-5}$ Torr) and exposure to water and pyridine vapour at pressures in the torr range. Both these adsorbates act as effective electron donors, shifting the flat band potential to more negative values. The field-effect mobility is found to be comparatively less affected through these transitions. Adsorption of the well known electron acceptor tetracyanoethylene (TCNE), is shown to cause depletion, with ppm levels of TCNE vapour in ambient atmosphere found to rapidly decrease the saturation current by over two orders of magnitude. The effect is only partially reversible on the hydrogen terminated surface, due to the accumulation of strongly bound TCNE molecules on the surface. In addition, oxidation of the H-terminated surface is seen to result in irreversible shifts in both the flat-band voltage and field-effect mobility. In order to passivate the surface from these irreversible processes, a photochemical gas phase reaction [4] with decene was used to form a decyl monolayer on the SOI(100)-H surface. Formation of this monolayer is found to result in a relatively small shift of threshold voltage and only a slight degradation of the field effect mobility. Decyl passivation only slightly decreases the response of the FET to TCNE adsorption while significantly improving the reversibility of the response. These results suggest that alkyl monolayer dielectrics formed by the gas phase photochemical method can function as good passivating dielectrics in field effect sensing applications.

[1] G. Dubey, G.P. Lopinski, and F. Rosei, *Appl. Phys. Lett.* **91**, 232111 (2007).

[2] G. Dubey, F. Rosei, and G.P. Lopinski, *Small* **6**, 2892 (2010).

[3] S. Cristoloveanu, and S. Williams, *IEEE Elec. Dev. Lett.* **13**, 102 (1992).

[4] B.J. Eves, and G.P. Lopinski, *Langmuir* **22**, 3180 (2006).

3:00pm **TF+EM+SS-ThA4 Micrometer- and Nanometer-Scale Patterning of Azide-Functionalized Self-assembled Monolayers on Gold and Aluminum Oxide Surfaces**, *O. El Zubir*, *I. Barlow*, *G. Leggett*, *N. Williams*, University of Sheffield, UK

Self-assembled monolayers (SAMs) have been prepared by the adsorption of [11-(4-azido-benzoylamino)-undecyl] phosphonic acid on aluminum oxide and by the adsorption of 11-(4-azido-benzoylamino)-undecylthiol. Exposure to near UV radiation causes elimination of nitrogen and the creation of a reactive nitrene species. Quantitative studies by X-ray photoelectron spectroscopy (XPS) and contact angle measurement show that the reaction is complete after an exposure of 20 J cm⁻². The reaction enables selective introduction of primary amines to the surface. By exposure of the azide under a solution of the amine, derivatization may be carried out with high efficiency, providing a simple pathway for the creation of a variety of multiple-component surface chemical patterns. Micropatterned surfaces were fabricated by exposure the SAMs to UV-laser ($\lambda=325$ nm) through a mask in presence of amines. Photopatterning was carried out at the nanometer scale by using scanning near-field photolithography (SNP) in which a scanning near-field optical microscope (SNOM) coupled to a UV laser ($\lambda=325$ nm) is utilized as the light source. Selective modification of azide terminated monolayers on aluminum oxide by protein-resistant molecules enabled the fabrication of protein nanopatterns that could be imaged by fluorescence microscopy.

3:40pm **TF+EM+SS-ThA6 Free-standing, SAM-based, Hybrid Biocompatible Nanomembranes for Biological Applications**, *N. Meyerbröker*, *W. Eck*, *M. Zharnikov*, Universität Heidelberg, Germany

Functional monomolecular films - so-called self-assembled monolayers (SAMs) - represent a broad platform for nanofabrication, sensor design, and molecular electronics, as well as a framework for Chemical Lithography, and a model system for organic interfaces and molecular, macromolecular and biological assemblies. These films can be prepared on different substrates which provide necessary support and guarantee the persistence of the 2D molecular assembly. Since the intermolecular interaction within the SAMs is relatively weak, such films cannot exist without support, dissipating into the individual constituents upon the separation from the substrate. However, as far as the individual molecules within a SAM can be cross-linked extensively by physical means such as electron irradiation, the resulting quasi-polymer film can be separated from the substrate and exist as a free-standing monomolecular membrane on its own. In this presentation we describe the formation of such free-standing membranes on the basis of aromatic SAMs. In contrast to the previous work, we used not only non-substituted but nitro- and nitrile-substituted SAM constituents which, due to either nitro-to-amine or nitrile-to-amine transformation, become chemically reactive after the irradiation treatment and can be subsequently coupled to further species. As such species we used oligo(ethylene glycol)-based molecules with a specific anchor group providing the coupling to the amine groups of the monomolecular template. After the attachment, these templates and respective hybrid membranes become protein-repelling and as such can be used as a non-disruptive and highly transparent support for proteins and cells in transmission electron microscopy (TEM) experiments. Whereas the ultimate thinness of this support guarantees a high imaging quality, protein-repelling ensures the lack of protein denaturing, which extends essentially the possibilities of TEM experiments in their specific application to sensitive biological targets.

4:00pm **TF+EM+SS-ThA7 Development of Nanoscale Heterostructures: From Single Component Nanostructures to Multicomponent Nanosystems**, *N. Chopra*, The University of Alabama, Tuscaloosa **INVITED**

Chemical vapor deposition (CVD) and solution synthesis was coupled to realize a unique surfactant-free approach for the direct nucleation of nanoparticles on 1-D nanostructures. Towards this end, skeleton nanostructures such as carbon nanotubes and oxide nanowires were successfully utilized as a selective nucleation sites for nanoparticles. Carbon nanotubes (CNTs)-Ni/NiO nanoparticles and oxide nanowires -(Au or Co₃O₄) nanoparticles were synthesized. Morphological evolution of nanoparticles as a function of various growth parameters was studied using

TEM, SEM, and XRD. New kinds of lattice relationships, interfaces, and morphologies were established. For example, CuO nanowire-Co₃O₄ nanoparticles showed unique optical characteristics leading to enhanced absorbance in visible light. Growth mechanisms of heterostructures revealed various competing phenomena at nanoscale including thermodynamic stability and chemical potential, and surface migration of nanoparticles on high curvature 1-D nanostructures as opposed to flat surface. These heterostructures also hold great promise as novel sensors and energy technologies.

4:40pm TF+EM+SS-ThA9 Physical and Electrical Characterization of Metal Incorporated SAM-based Molecular Electronic Junctions, S. Pookpanratana, M.A. Walsh, C.A. Richter, C.A. Hacker, National Institute of Standards and Technology

Molecular electronics is attractive for next-generation applications because of the flexibility in tailoring the organic functionality and the facile formation of uniform monolayers by using thiol-Au chemistry for self-assembly. Added functionality can be achieved by using thiol self-assembled monolayers (SAMs) containing terminal carboxylic acid functional groups to chelate with metal ions [1], and thus can incorporate d-orbital transition metals with the SAMs. One challenge in molecular electronics has been the reliable formation of a top contact to the organic layer. Fabrication techniques involving metal evaporation of the top contact often result in penetration to the substrate [2] or into the SAM [3], either of which influences the measured electrical properties across the junction. Here, we utilize flip chip lamination (FCL), a soft metallization technique by nanotransfer printing, to form a top contact onto SAMs on Au [4].

Based on previous work by Ulman et al. [5] and Allara et al. [6], we have incorporated metal ions (Cu and Ni) with mercaptohexadecanoic acid (MHA) and formed a molecular junction by FCL. SAMs of MHA were prepared on Au on Si and Au on polyethylene terephthalate (PET) substrates. The MHA/Au/Si was exposed to metal ion (M) containing solution. The M-MHA/Au/Si samples were then laminated to MHA/Au/PET to create a 'molecular sandwich' which resulted in the following structure: PET/Au/MHA-M-MHA/Au/Si where the PET substrate is removable.

The SAMs on Au were investigated by using X-ray photoelectron spectroscopy (XPS) and p-polarized reflection absorption infrared spectroscopy (p-RAIRS), and both methods confirm the initial presence of carboxylic acid on the (pre-FCL) surface. Successful incorporation of metal ions into the SAM were directly confirmed by XPS (occupying 30-50% of the -COOH sites), and indirectly by p-RAIRS with the appearance of C=O bands in an acid salt environment. Electrical and physical characterization (using backside p-RAIRS and near edge X-ray absorption fine structure (NEXAFS)) measurements to investigate the monolayer after FCL are currently ongoing. With these results, we are able to obtain a thorough picture linking electrical properties with physical characterization of the buried molecular junctions.

- [1] A. C. Templeton et al., *Langmuir*, 2000, 16, 6682-6688.
- [2] A. V. Walker et al., *J. Am. Chem. Soc.*, 2004, 126, 3954-3963.
- [3] C. A. Richter et al., *Solid-State Electron.*, 2006, 50, 1088-1096.
- [4] M. Coll et al., *J. Am. Chem. Soc.* 2009, 131, 12451-12457.
- [5] S. D. Evans et al., *J. Am. Chem. Soc.*, 1991, 113, 5866-5868.
- [6] T. A. Daniel et al., *Langmuir*, 2007, 23, 638-648.

5:00pm TF+EM+SS-ThA10 Examining the Role of Laminin-Derived Peptides in Neuronal Attachment, N.A. LaFranzo, J.A. Maurer, Washington University in St. Louis

Laminin-1 is a 900kD glycoprotein that is a major component of the extracellular matrix (ECM). Laminin is known to be involved in many cellular processes including cell adhesion, migration and differentiation *in vivo* and is often used in *in vitro* experiments to encourage neuronal attachment. While laminin contains some integrin-receptor binding sites, multiple domains on the protein including the peptide sequences IKVAV, YIGSR and RGD have also been shown to bind to non-integrin neuronal receptors, encourage cell adhesion, and encourage neurite outgrowth in the absence of the full protein structure. However, previous experiments performed using these peptides as substrates for neuronal culture fail to consider the effects of excretion of the cells own ECM proteins onto the surface, which we have shown can occur on surfaces with high peptide concentrations. By utilizing self-assembled monolayers (SAMs), we have created a substrate that prevents the non-specific adsorption of proteins excreted by neurons, while introducing a low-concentration of the peptide sequences to encourage neuronal attachment.

A pair of alkane-thiol monomers for assembly on a gold substrate have been designed which contain a tetra-ethylene glycol moiety at the tail to prevent

the non-specific adsorption of proteins. One of the monomers is terminated with an azide moiety that can be used to specifically attach molecules with an alkyne group by a copper-mediated azide-alkyne cycloaddition (CuAAC) reaction, also known as the "click" reaction. By introducing 5-pentynoic acid at the N-terminus of each of the peptides during synthesis, we have introduced a bioorthogonal attachment point for reaction with the azide-terminated monomers on the surface. Once prepared, these surfaces have been confirmed to be resistant to adsorption of proteins by quartz-crystal microbalance (QCM) experiments. Primary culture neurons dissected from embryonic mice have been cultured on the surface and the effects of the peptides on neurite outgrowth have been quantified. To better understand the role of these peptides in cell adhesion, neurons transfected with a plasmid encoding EGFP-vinculin or EGFP-paxillin have been cultured on the surface and the focal adhesion morphologies have been observed in live-cell imaging experiments. These results are compared to those observed for a surface where the full laminin protein has been adsorbed. Together, these experiments help to design a surface resistant to non-specific protein adsorption that allows for neuronal adhesion, sheds light on laminin-mediated attachment, and aids in developing better small-molecule mimics of receptor-mediated cellular adhesion.

5:20pm TF+EM+SS-ThA11 Contact-Free Electrical Characterization of Molecular Layers using CREM, H. Cohen, Weizmann Inst. of Science, Israel

While generally recognized as a powerful analytical tool, XPS is insensitive to hydrogen atoms and, in many cases, to fine variations in the environment of carbon atoms. As such, XPS characterization of organic molecular layers is rather limited, in particular under demands for high overlayer quality. On the other hand, a recent XPS-based technique for chemically resolved electrical measurements (CREM) proposes high sensitivity to even small amounts of defects or organization imperfections [1,2].

Here, CREM application to monolayers self-assembled on metallic or semiconducting substrates is overviewed, demonstrating some of the unique capabilities offered by this non-contact probe. Damage evolution under irradiation is specifically discussed; two of its extreme limits being modeled, yielding the effect of corresponding defect sites on the CREM-derived I-V curves. Potential applications to molecular electronics, approaching *atomic* resolution in the electrical data, will be discussed.

References

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- H. Cohen, *Applied Physics Letters* **85**, 1271 (2004).

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